

Preparation and microstructure evolution of diboride ultrafine powder by sol–gel and microwave carbothermal reduction method

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Abstract Titanium diboride ultrafine powder was prepared from sucrose, tetrabutyl titanate and boric acid by the sol–gel and microwave carbothermal reduction method. The influence of reaction temperature, ratio of Ti to C and Ti to B on the synthesis of titanium diboride was studied. The results indicated that the carbothermal temperature, the content of carbon and the amount of H_3BO_3 show obvious effects on the formation of TiB_2 . 1,300 °C was the optimum synthesis temperature and pure TiB_2 could be prepared. The microstructure of prepared TiB_2 was investigated by field emission-scanning electron microscopy (FE-SEM), which results showed that the crystalline size of the prepared titanium diboride at 1,300 °C was about 3–5 μm . The quantities of the crystalline phases of the powders prepared at different temperatures were analyzed by Rietveld refinement method.

Keywords Sol–gel · Microwave · Carbothermal · Reduction · Titanium diboride · Powders

1 Introduction

Titanium boride combines a lot of important characteristics, i.e., high melting point (about 3,526 °C), high elastic modulus (about 541 GPa), high hardness, good chemical inertness, and high wear resistance, that make it a promising candidate for high temperature structural materials [1, 2]. Those properties also make TiB_2 attractive in many fields of engineering, such as cutting tools, ballistic armor,

dispersoid for metal/ceramic matrix composite, and as a cathode for electrochemical reduction of aluminum (Hall–Heroult cell) with a possibility of reduced cell voltage [3].

TiB_2 powders can be usually synthesized by following methods [4–12]; (i). By carbothermic, aluminothermic, silicothermic or magnesiothermic reduction of TiO_2 – B_2O_3 mixtures at high temperature usually over 1,600 °C; (ii). By electrolysis of fused salts containing mineral rutile and boric oxide dissolved in mixed electrolytes; (iii). By the reduction of TiO_2 with carbon and boron carbide; (iv). By Self-propagating-high-temperature synthesis (SHS) technique. However, it is always necessary to have a high temperature and a long production period in those methods, and the synthesized powders usually have a relatively large crystallite size and poor sinterability.

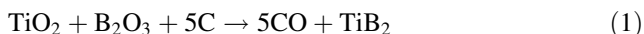
The microwave sintering method has been developed for fabricating metals, ceramics, and composites [13–15]. Compared with conventional sintering process, the microwave sintering technique allows lower sintering temperature and shorter soaking time.

Recently, the preparation of ultrafine powders has received much attention as it can improve the microstructure of the sintered sample, and enhance its mechanical properties. The sol–gel process is a well-known chemical route to prepare oxide-based materials. Moreover, the use of molecular precursors and the control of the synthesis conditions make it possible to prepare homogeneous and pure multicomponent systems. However, to the knowledge of authors, there is no report on the preparation of TiB_2 by a homogeneous sol–gel and microwave heating process. The aim of the present work was to investigate the low temperature preparation of TiB_2 ultrafine powder using a novel approach of combining sol–gel and microwave carbothermal reduction.

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2 Experimental procedure

Starting materials utilized in present paper were analytical reagent grade tetrabutyl titanate (≥ 99.8 Wt%, Beijing Chem. Co. Ltd., Beijing, China, $C_{16}H_{36}O_4Ti$), H_3BO_3 (≥ 99 Wt%, Beijing Chem. Co. Ltd., Beijing, China), sucrose (≥ 99 Wt%, Beijing Chem. Co. Ltd., Beijing, China, $C_{12}H_{22}O_{11}$). TiB_2 is obtained by the following reaction,



A stoichiometric amount of H_3BO_3 was dissolved in distilled water, then a stoichiometric amount of sucrose was added, and after complete mixing, a homogenous transparent solution was achieved. The solution was then slowly mixed with tetrabutyl titanate precursor to get the gel; and the gel was heated in a temperature range of 120–140 °C for 24 h to get a dried gel. Finally, the dried gel precursor was fired in microwave furnace (The sketch of microwave heating furnace is shown in Fig. 1. Model: MW-L0316V, 3 kW, 2.45 GHz, by Changsha Longtech CO., Ltd, Hunan province, China) at 900–1,300 °C for 2 h in flowing Ar atmosphere (Ar purity = 99.9999 wt%) to obtain ultrafine TiB_2 powder. The heating rate was about 20 °C min^{-1} , the plateau reaction temperature could be held within $\pm 5\text{ °C}$. The gas outlet valve was normally opened on heating and closed at 600 °C on cooling. Two series of specimens were prepared: (1). in one series (designated as TC series), the molar ratio of TiO_2/B_2O_3 in starting precursor was 1:1 (theoretical ratio by Eq. 1), and the amount of carbon was changed. (2). the molar ratio of TiO_2/C in the starting precursor was 1:5 (theoretical ratio by Eq. 1), and the amount of B_2O_3 was changed.

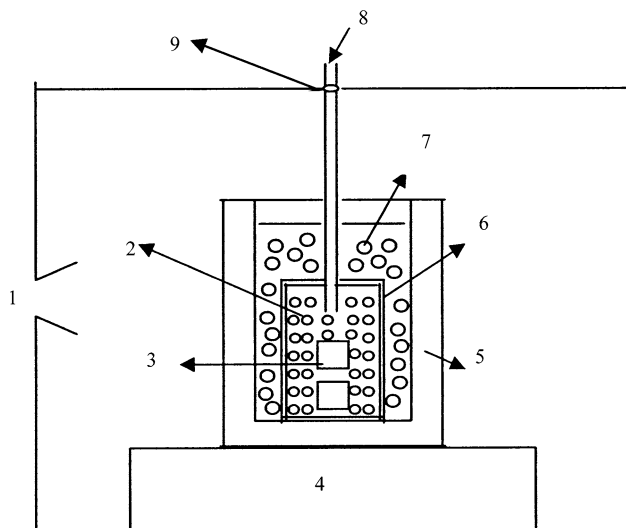


Fig. 1 Sketch of microwave heating furnace. (1) Waveguide (2) SiC powders (3) Samples (4) Rotating platform (5) Furnace lining (6) Alumina crucible (7) Alumina hollow sphere (8) High purity Ar (9) Infra-red temperature measurement system

X-ray diffraction patterns were recorded from 20° to 100° (2θ) with a step width of 0.02° , using a Philips X'Pert PRO diffractometer (Cu K_α radiation, Ni filter and silicon internal standard, 40 kV, 40 mA, time per step 3.80 s). The Rietveld refinement method, an established way for the quantitative determination of crystalline phases, was used to refine the structure of the phases in the samples. The PANalytical X'pert Highscore plus program has been used for the refinement analysis. The microstructure of the samples was directly studied using a field emission scanning electron microscopy (FESEM; JSM-6700F, JEOL, JAPAN) equipped with energy-dispersive spectroscopy (EDS; Oxford, UK) without carbon/gold coating.

3 Results and discussions

Figure 2 shows the XRD patterns of TC series samples with different $TiO_2:B_2O_3:C$ ratio fired at 900–1,300 °C. It

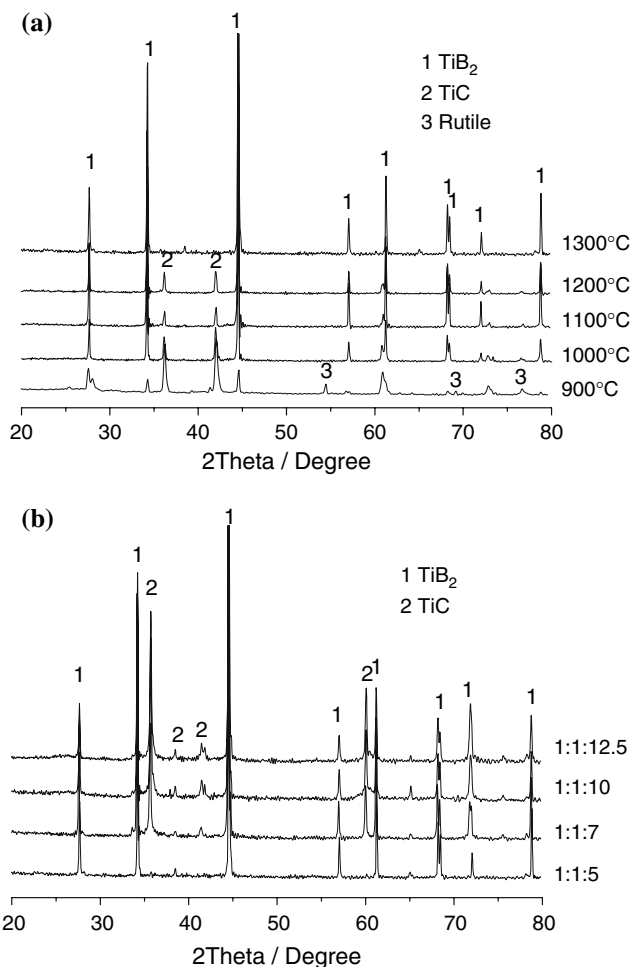


Fig. 2 XRD results of TiB_2 prepared with different amount of carbon (TC specimens). (a) $TiO_2:B_2O_3:C = 1:1:5$ molar ratio (b) 1,300°C/2 h. (1: TiB_2 JCPDS 35-0741; 2: TiC JCPDS 32-1383; 3: $TiO_2(R)$ JCPDS 21-1276)

indicates that the inception formation temperature of TiB_2 by sol–gel and microwave carbothermal reduction way is about 900 °C. The extent of TiB_2 formation is influenced by amount of C addition and annealing temperature. For specimens with theoretical carbon addition (TC-1), there is an increase in TiB_2 formation with temperature rise up to 1,300 °C, and pure TiB_2 crystal phase can be prepared at 1,300 °C (Fig. 2a). This temperature is much lower than that of the conventional method (over 1,500 °C) [16]. Excess amount of carbon plays a negative effect on the preparation of pure TiB_2 , it can be concluded from the XRD patterns showed in Fig. 2b.

Table 1 shows the preparation condition and the content of phase composition of TC series specimens with different carbon annealed at 900–1,300 °C. From the results, it can be seen: (1). The amount of TiC formed increase with carbon content, and decreases with temperature rise. It is interesting to note that TiC may be a transitory phase; the temperature of its formation commences at about 900 °C. For specimens with theoretical carbon addition (TC-1), it is perhaps transformed to formation TiB_2 at high temperature (1,300 °C). (2). Over 1,000 °C, TiO_2 phase (rutile) can not be observed, this shows that the carbothermal reduction process is complete at this temperature. (3). The lattice parameter of TiB_2 decreased with increasing temperature and decreasing carbon content, especially in the parameter of a. The lattice parameter of TiB_2 (TC-1 specimen) at 1,300 °C is $a = b = 3.027(3)\text{\AA}$ and $c = 3.230(2)\text{\AA}$, which is little different with that of the pure tetragonal TiB_2 phase ($a = b = 3.028\text{\AA}$ and $c = 3.228\text{\AA}$, ICSD reference code 98–001–3159).

Figure 3 shows the XRD patterns of TB series samples fired at 900–1,300 °C. It illustrates that Pure TiB_2 is prepared for all the TB series specimens at 1,300 °C (Fig. 3a).

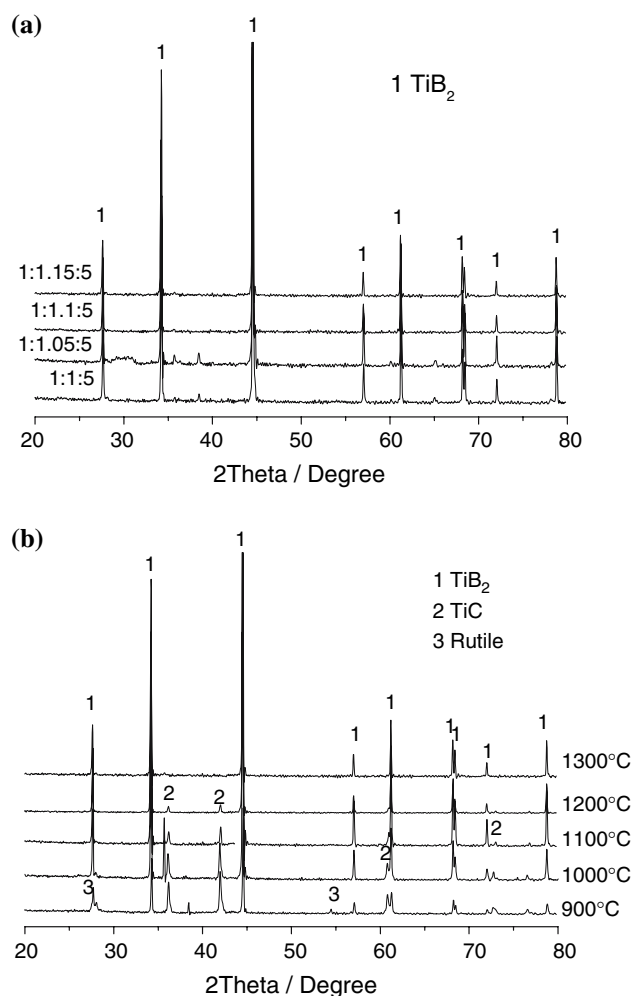


Fig. 3 XRD results of TiB_2 prepared with different amount of boric acid (TB specimens) (a) 1,300°C/2 h (b) $TiO_2:B_2O_3:C = 1:1.15:5$ molar ratio). (1: TiB_2 JCPDS 35–0741; 2:TiC JCPDS 32–1383; 3: $TiO_2(R)$ JCPDS 21–1276)

Table 1 Parameters and composition content of TiB_2 preparation with different amount of carbon at 900–1,300 °C (TC series specimens)

Sample	$TiO_2:B_2O_3:C$ /molar ratio	T/°C	TiB ₂ Cell parameter		Content of TiB ₂ /%	Content of TiC/%	Content of Rutile/%
			a = b/Å	c/Å			
TC-1	1:1:5.0	1,300	3.027(3)	3.230(2)	100(.0)	0(.0)	0(.0)
		1,200	3.027(9)	3.229(7)	94(.5)	5(.5)	0(.0)
		1,100	3.027(6)	3.229(1)	92(.5)	7(.5)	0(.0)
		1,000	3.028(5)	3.229(9)	79(.7)	20(.3)	0(.0)
		900	3.029(5)	3.230(4)	18(.8)	59(.3)	21(.9)
TC-2	1:1:7.5	1,300	3.026(9)	3.229(4)	90(.3)	9(.7)	0(.0)
		1,200	3.028(9)	3.230(1)	93(.1)	6(.9)	0(.0)
		1,100	3.028(7)	3.229(4)	95(.9)	4(.1)	0(.0)
		1,000	3.031(3)	3.231(8)	75(.0)	25(.0)	0(.0)
		900	3.029(7)	3.231(1)	13(.4)	55(.0)	31(.5)
TC-3	1:1:10	1,300	3.028(4)	3.229(9)	85(.6)	14(.4)	0(.0)
TC-4	1:1:12.5	1,300	3.028(8)	3.230(1)	77(.9)	22(.1)	0(.0)

When B₂O₃ addition is 15% (molar ratio) more than that theoretical content and the annealing temperature is 900 °C, the extent of TiB₂ formation is more than 50% (Table 2). This indicates that for synthesizing TiB₂ by tetrabutyl titanate, H₃BO₃ and sucrose, the excessive amount of B₂O₃ is effective in promoting TiB₂ preparation at low temperature (Fig. 3b).

SEM images of the synthesized TiB₂ powders at 1,300 °C for 2 h are shown in Fig. 4. From the SEM images (Fig. 4a), the granular particle sizes of the synthesized TiB₂ powders distribute over 3–5 μm, and agglomerations appear in the samples. Some of the particles are plate-like, clear growth steps (Fig. 4b) are observed in them. And the grain growth of those particles

Table 2 Parameter and composition content of TiB₂ preparation with different amount of boric acid at 900–1,300°C (TB series specimens)

Sample	TiO ₂ :B ₂ O ₃ :C/molar ratio	T/ °C	TiB ₂ Cell parameter		Content of TiB ₂ /%	Content of TiC/%	Content of Rutile/%
			a = b/Å	c/Å			
TB-1	1:1.05:5	1,300	3.027(3)	3.229(8)	100(.0)	0(.0)	0(.0)
		1,200	3.027(7)	3.229(5)	93(.9)	6(.1)	0(.0)
		1,100	3.027(9)	3.229(1)	96(.8)	3(.2)	0(.0)
		1,000	3.028(6)	3.229(5)	82(.9)	17(.1)	0(.0)
		900	3.029(9)	3.231(1)	20(.2)	57(.3)	22(.5)
TB-2	1:1.10:5	1,300	3.027(0)	3.230(1)	100(.0)	0(.0)	0(.0)
		1,200	3.028(0)	3.229(5)	94(.5)	5(.5)	0(.0)
		1,100	3.027(5)	3.228(9)	86(.8)	13(.2)	0(.0)
		1,000	3.028(7)	3.229(8)	83(.6)	16(.4)	0(.0)
		900	3.029(5)	3.230(7)	33(.7)	49(.3)	17(.0)
TB-3	1:1.15:5	1,300	3.027(1)	3.229(5)	100(.0)	0(.0)	0(.0)
		1,200	3.027(8)	3.228(9)	96(.1)	3(.9)	0(.0)
		1,100	3.027(8)	3.229(3)	96(.2)	3(.8)	0(.0)
		1,000	3.028(3)	3.229(5)	85(.4)	14(.6)	0(.0)
		900	3.029(5)	3.230(5)	57(.8)	34(.6)	7(.5)

Fig. 4 SEM photograph and EDS results of TC-1 sample prepared at 1,300°C by sol-gel and microwave carbothermal method (a) granular-shaped TiB₂ particles (b) growth steps along the (a–b) plane of TiB₂ particles (c) growth steps along the a–b, and c plane of TiB₂ particles (d) EDS results (atomic ratio%) of the selected points in Fig.4a

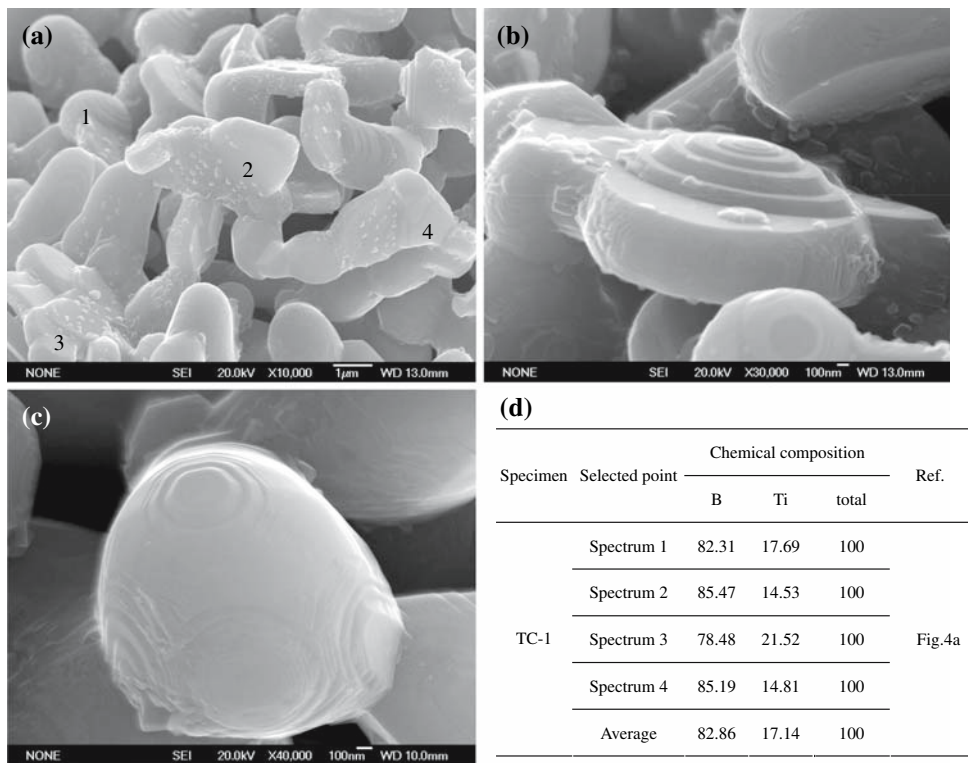
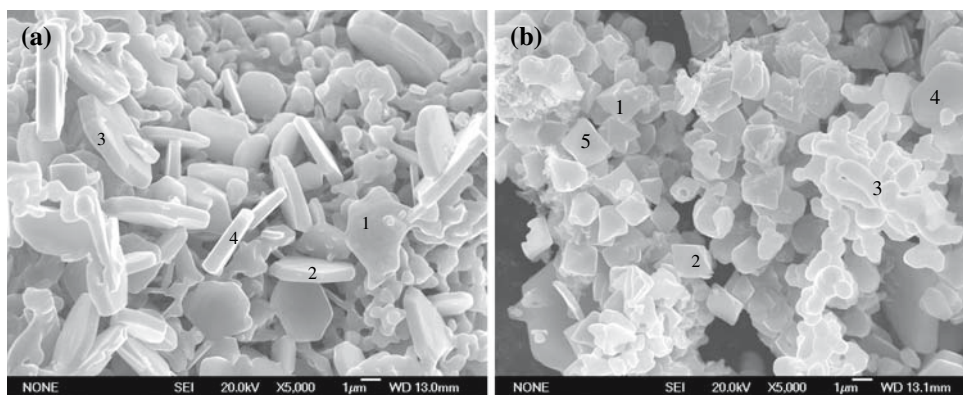


Fig. 5 SEM photograph and EDS results of TC-1 sample prepared at 1,100°C by sol-gel and microwave carbothermal method (a) hexagonal-shaped TiB₂ particles (b) octahedral-shaped TiC and granular-shaped TiB₂ particles (c) EDS results (atomic ratio%) of the selected points in Fig.5a, b



(c)

Specimen	Selected point	Chemical composition				Ref.
		B	Ti	C	total	
TC-1	Spectrum 1	77.71	22.29	0.00	100	Fig.5a
	Spectrum 2	87.19	12.81	0.00	100	
	Spectrum 3	78.73	21.27	0.00	100	
	Spectrum 4	83.43	16.57	0.00	100	
	Average	81.77	18.23	0.00	100	
TC-1	Spectrum 1	0.00	37.38	62.62	100	Fig.5b
	Spectrum 2	0.00	39.62	60.38	100	
	Spectrum 3	81.67	18.33	0.00	100	
	Spectrum 4	83.21	16.79	0.00	100	
	Spectrum 5	0.00	66.99	33.01	100	

not only occurred along the *a*–*b* plane but also along the *c*-axis of the TiB₂ unit cell, which growth of the plate-like crystals along the *c*-axis is evidenced in Fig. 4c. The growth of these plate-like crystals was driven by the reduction in the substantial particle surface energy at the beginning of the growth process. Subsequently, the crystal growth of a, b and c-axis became less efficient when the effective particle surface area was decreased, and then those plate-like crystals joined together to form big granular particle with growth steps (Fig. 4a). EDS analysis (Fig. 4d) of the granular particles in Fig. 4a shows the only presence of Ti and B, which undoubtedly indicates that the pure TiB₂ powders are prepared at 1,300 °C.

Figure 5 shows the SEM images of the synthesized powders at 1,100 °C for 2 h. Three kinds of particles with different shape were found, the first ones is hexagonal – shaped (as the selected points in Fig. 5a), its crystallite

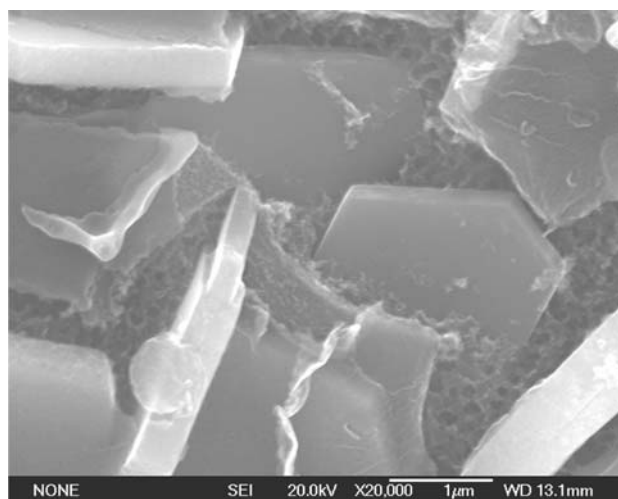


Fig. 6 SEM photograph of TC-1 sample prepared at 1,000°C by sol-gel and microwave carbothermal method

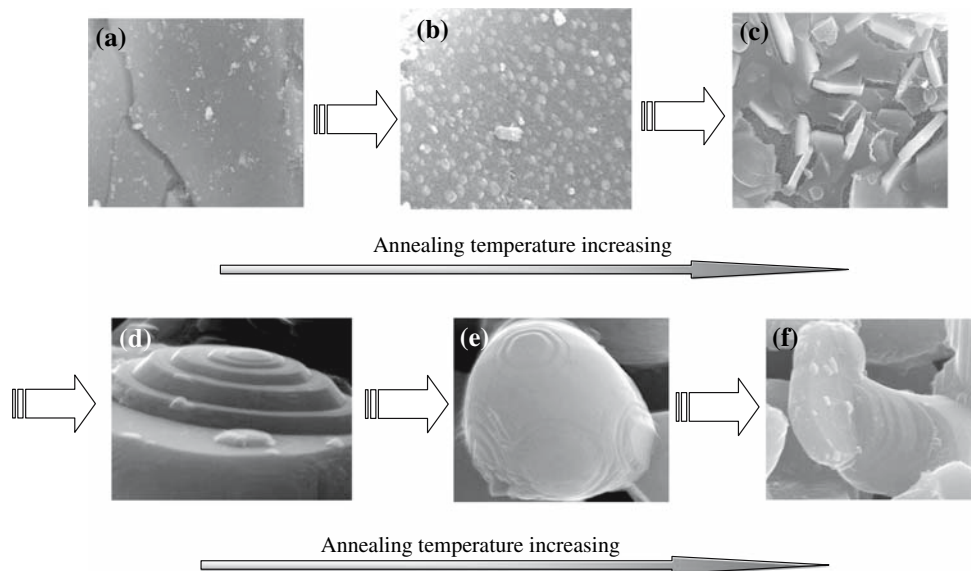


Fig. 7 Microstructure morphology evolution of TiB_2 crystal at different temperature. (a) Gel (b) Small TiB_2 crystal (c) Plate-like TiB_2 particles (d) Plate-like TiB_2 particles with crystal growth in one direction (e) Granular particles with crystal growth in all direction (f) Big column-like particles

sizes mainly distribute over 2–4 μm , and the EDX analysis (Fig. 5c) shows that those particles are TiB_2 . This shape is in accordance with the theoretical crystal structure of TiB_2 . The second ones is octahedral-shaped (as the selected point 1, 2 and 5 in Fig. 5b), its EDX analysis (Fig. 5c) indicates that these particles are TiC. The third ones is granular with size about 1 μm (as selected point 3 and 4 in Fig. 5b), the EDS results (Fig. 5c) demonstrates it is also TiB_2 .

The growth of lamellar TiB_2 crystals along a favored orientation with a lateral growing mechanism is also shown in Fig. 6. From this figure, it can be clearly seen that TiB_2 nucleated and grew in a pool of “amorphous phase”. “The amorphous phase” was consumed through the grain growth, and those small grains were subsequently joined together to form plate-like crystals with an orientation parallel to the pellet surface. The “amorphous phase” is undetectable by XRD due to its non-crystalline nature. Based on the SEM results of Figs. 4–6, a possible microstructure transformation of the prepared TiB_2 crystals can be proposed as shown in Fig. 7.

4 Conclusions

Ultrafine TiB_2 was formed by sol–gel and microwave carbothermal reduction process using tetrabutyl titanate, H_3BO_3 and sucrose as studying materials. The initial crystallization temperature of the TiB_2 powder is about 900 $^\circ\text{C}$, whereas that of the fully crystallized TiB_2 appeared at about 1,300 $^\circ\text{C}$. The carbothermal temperature,

the content of carbon and the amount of H_3BO_3 show obvious effects on the formation of TiB_2 .

The principal factors influencing ultrafine TiB_2 powder synthesis are: ① Formulation. For promoting ultrafine TiB_2 formation at lower temperatures, use of tetrabutyl titanate, H_3BO_3 and sucrose is recommended at $\text{TiO}_2\text{:B}_2\text{O}_3\text{:C} = 1\text{:}1\text{:}5$ molar ratios. ② Temperature. The suitable firing temperature is 1,300 $^\circ\text{C}$. The TiB_2 powders prepared at 1,300 $^\circ\text{C}$ are granular with size 3–5 μm .

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